



## Short communication

## Ultramicroporous carbon as electrode material for supercapacitors

Bin Xu<sup>a,\*</sup>, Shanshan Hou<sup>b</sup>, Hui Duan<sup>b</sup>, Gaoping Cao<sup>a</sup>, Mo Chu<sup>b</sup>, Yusheng Yang<sup>a</sup><sup>a</sup> Research Institute of Chemical Defense, Beijing 100191, China<sup>b</sup> School of Chemical and Environmental Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China

## H I G H L I G H T S

- ▶ PVDF-derived carbon has a surface area of 1012 m<sup>2</sup> g<sup>−1</sup> with pores of 0.55 nm.
- ▶ The carbon is investigated as electrode material for supercapacitors.
- ▶ It presents a high volumetric capacitance of 218 F cm<sup>−3</sup> in aqueous electrolytes.
- ▶ Its capacitance in non-aqueous electrolytes is very small (<7 F g<sup>−1</sup>).

## A R T I C L E I N F O

## Article history:

Received 21 May 2012

Received in revised form

27 November 2012

Accepted 29 November 2012

Available online 5 December 2012

## Keywords:

Supercapacitor

Porous carbon

Ultramicropore

Capacitance

## A B S T R A C T

Poly(vinylidene fluoride)-derived ultramicroporous carbon with a specific surface area of 1012 m<sup>2</sup> g<sup>−1</sup> and a very narrow pore-size distribution peaked at 0.55 nm is investigated as electrode material for supercapacitors. The unique microstructure features enable the carbon to present not only a high gravimetric capacitance (264 F g<sup>−1</sup>) but also a high electrode density (0.826 g cm<sup>−3</sup>), resulting in an outstanding high volumetric capacitance of 218 F cm<sup>−3</sup> in 6 mol L<sup>−1</sup> KOH aqueous electrolytes. However, the carbon shows a very small capacitance of less than 7 F g<sup>−1</sup> in 1 mol L<sup>−1</sup> Et<sub>4</sub>NBF<sub>4</sub>/PC, which implies the pores are too small to be accessible even for the desolvated ions in the non-aqueous electrolyte.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

As a promising energy-storage device with high power density and long cycle life, supercapacitor has recently attracted great interests due to its wide application in memory back-up systems, uninterruptible power sources, electric vehicles and renewable energy sources, etc. Porous carbon materials are the most widely used electrode materials because of their high surface area, controllable pore size and low cost. The porous carbon-based supercapacitor is called electric double layer capacitor (EDLC), which stores energy based on the charge separation at the electrode/electrolyte interface. As the energy density of the commercial EDLCs is only 3–5 Wh kg<sup>−1</sup>, much lower than that of the secondary batteries, current EDLC research is mainly focused on increasing the energy density [1–3]. Therefore, it is desired to develop advanced carbon with high capacitance, which requires the carbon to have

not only high surface area but also optimized pore size. Activated carbons prepared by physical or chemical activation usually have a wide pore size distribution from ultramicropores (<0.7 nm), micropores (<2 nm) to mesopores (2–50 nm) and macropores (>50 nm). As only the surface of the pores that the ions can access can contribute to double layer capacitance, the pore size must large enough to be accessible for the ions. On the other hand, for practical application, the volumetric capacitance is of great importance, requiring a high density of the carbons [4,5]. As large pore size is usually in contradiction with high surface area and high density, the optimized pore size should large enough to be accessible for the ions, but small enough to ensure a large surface area and high density.

For aqueous EDLCs, since the size of a single nitrogen molecule is similar to that of hydrated OH<sup>−</sup> or K<sup>+</sup>, those micropores that can adsorb nitrogen molecules at 77 K are also available for the electro-adsorption of simple hydrated ions [6]. In principle, it is believed that the pores larger than 0.5 nm could be electrochemically accessible for aqueous electrolytes [7–9]. As for non-aqueous electrolytes, previously, it has been concluded that pores under 1 nm is too small

\* Corresponding author. Tel./fax: +86 10 66705840.

E-mail addresses: [xubinn@sohu.com](mailto:xubinn@sohu.com), [binxumail@163.com](mailto:binxumail@163.com) (B. Xu).

to be accessible as the solvated ions are about 1–2 nm [10,11]. A pore size distribution in the range of 2–5 nm, which is larger than the size of two solvated ions, was then identified as a way to improve the energy density and the power capability of the carbons [12]. However, some recent studies have demonstrated that subnanometer pores in 0.65–1 nm can also be accessible and a maximum capacitance is obtained for an average pore size of 0.7 nm, in a good agreement with the desolvated ion size [13–15]. It is suggested that desolvated ions instead of solvated ions are stored in such small pores. According to this theory, it can deduce that the pores smaller than 0.65 nm seem to be not useful, as it is too small to be accessible even for the desolvated ions. However, no evidence has clearly confirmed it. One of the probably reasons is the absence of carbons which have pores of such small size with unimodal, narrow distribution as a model material.

Recently, we have simply prepared a microporous carbon with a surface area of 1012 m<sup>2</sup> g<sup>-1</sup> by the pyrolysis of poly(vinylidene fluoride) (PVDF) at high temperature without activation and any other additional processes [16]. As the pores are unimodal at 0.55 nm with a very narrow distribution, the carbon seems to be a good candidate material for high capacitance aqueous EDLCs, as well as a good model material to investigate the capacitive behavior of the pores smaller than 0.65 nm in non-aqueous electrolytes.

In this context, herein, we investigate the electrochemical capacitive performances of the PVDF-derived carbon in both aqueous and non-aqueous electrolytes. The carbon presents an outstanding high volumetric capacitance of 218 F cm<sup>-3</sup> in 6 mol L<sup>-1</sup> KOH, approving that 0.55 nm is an optimized pore size for high capacitance aqueous EDLCs. However, the very small value of capacitance (<7 F g<sup>-1</sup>) in 1 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub>/PC electrolytes implies pores of 0.55 nm are too small to be accessible even for the desolvated ions in non-aqueous electrolytes.

## 2. Experimental

As reported in our previous paper [16], the ultramicroporous carbons were simply prepared by carbonization homogeneous PVDF (Kynar 761, Arkema Co.) at 600–900 °C for 1 h under nitrogen protection without activation and any other additional processes. The pores are created from thermal decomposition of PVDF by releasing HF, which is a corrosive and toxic gas. To avoid its hazard, the used furnace tube and the boat for loading PVDF are all made of stainless steel, and some CaO were placed in the outer side of the furnace tube to absorb the released HF.

N<sub>2</sub> (77 K) adsorption was conducted from relative pressure  $p/p_0$  of 10<sup>-6</sup>–1 to assess the porosity and surface area data of the carbons using a Micromeritics ASAP 2020. Before measurements, the samples were outgassed at 300 °C for 12 h. The specific surface area and pore size distributions were calculated by the conventional Brunauer–Emmett–Teller (BET) method and density functional theory (DFT) method for slit shaped pores provided by ASAP 2020 data software version 3.04 from the N<sub>2</sub> (77 K) adsorption isotherms, respectively. To ensure the accuracy for such small pores, CO<sub>2</sub> (273 K) adsorption was conducted from relative pressure  $p/p_0$  of 10<sup>-6</sup>–0.03, and the pore size distributions are also calculated by same method from CO<sub>2</sub> (273 K) adsorption isotherms.

In order to evaluate the electrochemical performances of the as-prepared PVDF-derived carbons in EDLCs, a mixture of 87 wt% of carbon, 10 wt% of acetylene black and 3 wt% of PTFE binder was pressed into pellets of 11 mm in diameter. Nickel foam and aluminum mesh were used as current collectors for EDLCs with 6 mol L<sup>-1</sup> KOH and 1 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub>/PC as electrolytes, respectively. After pressed with the current collector, the carbon electrodes were obtained. Then the electrodes were dried under vacuum at 120 °C for 6 h. The apparent density  $\rho$  (cm<sup>3</sup> g<sup>-1</sup>) of the

carbon pellet is measured according to the formula  $\rho = m/Sd$ , where  $m$  is the mass of a dried carbon pellet (g),  $S$  and  $d$  are the area (cm<sup>2</sup>) and thickness (cm) of the carbon pellet, respectively.

Button-type symmetrical capacitor was assembled with two carbon electrodes using 6 mol L<sup>-1</sup> KOH aqueous solutions and 1 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub>/PC as electrolytes, respectively. For the capacitor with the later electrolyte, the assemble process is accomplished in an Ar-filled glovebox (M. Braun LabMaster 130, H<sub>2</sub>O < 5 ppm). The cyclic voltammetry (CV) was recorded on a Solartry 1280B electrochemical workstation. The galvanostatic charge/discharge was carried out on an Arbin BT2000 cell tester. The cutoff charge voltage for the capacitor using 6 mol L<sup>-1</sup> KOH and 1 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub>/PC was set as 0–1.0 V and 0–2.5 V, respectively. The specific capacitance ( $C$ ) of a single electrode was determined with the formula  $C = 4It/\Delta Vm$  [17], where  $I$  is the discharge current (A),  $t$  is the discharge time (s),  $\Delta V$  is the potential change in discharge (V) and  $m$  is the total mass (g) of the active material in both electrodes.

## 3. Results and discussion

Fig. 1a shows the nitrogen (77 K) adsorption/desorption isotherms and DFT pore size distribution of the PVDF-derived carbons prepared at different carbonization temperatures. All the

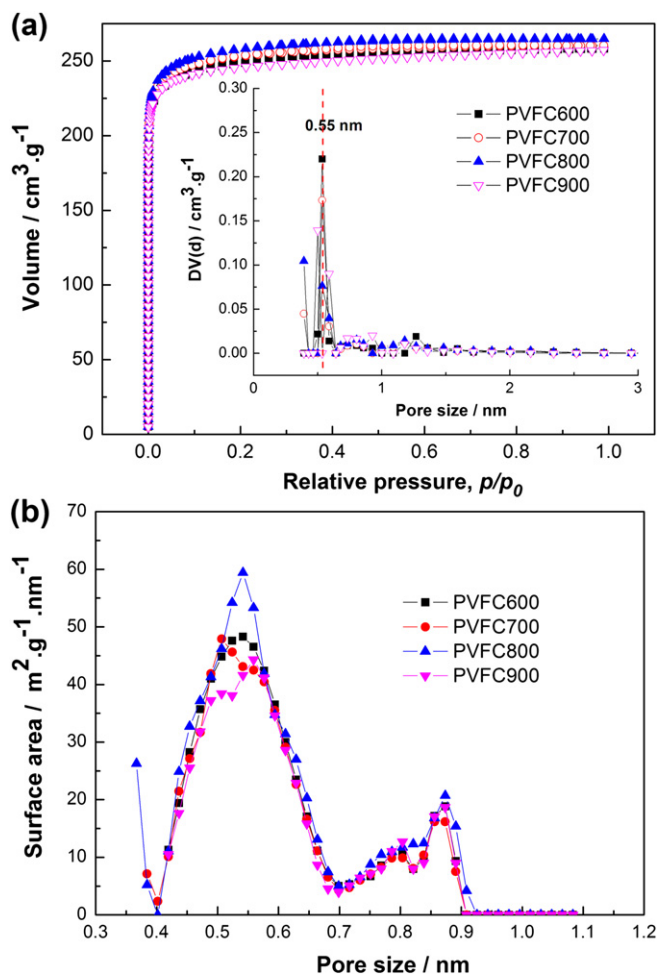


Fig. 1. (a) Nitrogen (77 K) adsorption/desorption isotherms, inset: Pore size distribution calculated from nitrogen (77 K) adsorption isotherms by DFT method for slit shaped pores; (b) pore size distribution calculated from CO<sub>2</sub> (273 K) adsorption isotherms by DFT method for slit shaped pores.

carbons exhibit typical type I nitrogen adsorption/desorption isotherms. The knee of the isotherms appears at very low relative pressure ( $p/p_0 < 0.05$ ) and the plateau is fairly flat, indicating highly microporous carbons. As listed in Table 1, the BET surface area and pore volume of the carbons are about  $1000 \text{ m}^2 \text{ g}^{-1}$  and  $0.40 \text{ cm}^3 \text{ g}^{-1}$ , respectively, independent on the carbonization temperature. The DFT pore size distribution curves indicate all of the carbons are highly ultramicroporous with unimodal, very narrow pore size distribution peaked at 0.55 nm.

To ensure the accuracy for such small pores, the pore size distributions of the carbons are also calculated from  $\text{CO}_2$  (273 K) adsorption isotherms by the same method. As shown in Fig. 1b, except a few pores in 0.7–0.9 nm, the pores of the carbons distribute predominated in 0.4–0.7 nm with a peak at 0.55 nm. This confirms that the carbons are ultramicroporous with pores of 0.55 nm.

The electrochemical capacitive performances of the PVDF-derived carbons in  $6 \text{ mol L}^{-1}$  KOH aqueous solutions were measured in a symmetrical two-electrode cell [17]. As shown in Fig. 2a, the CV curves of the carbons between 0 and 1 V at a scan rate of  $2 \text{ mV s}^{-1}$  all show rectangular-like shapes, implying capacitive behavior. As listed in Table 1, the specific capacitance of the carbons calculated by galvanostatic charge/discharge at a current load of  $0.05 \text{ A g}^{-1}$  reaches  $197\text{--}265 \text{ F g}^{-1}$ , confirming that the ultramicropores of 0.55 nm in size are large enough to be accessible for the ions in aqueous electrolytes.

Besides of surface area and pore size, the surface chemistry also has an important effect on the electrochemical performance of the carbons. It has been indicated that the presence of heteroatoms on the carbon surface such as oxygen [18], nitrogen [19], phosphorus [20] and chloride [5] are usually advantageous, as they can considerably contribute to an additional pseudo-capacitance as well as improve the wettability with the electrolyte. Although the BET surface area of the PVDF-derived carbon is only  $1000 \text{ m}^2 \text{ g}^{-1}$ , independent on the carbonization temperature, the capacitance of the carbon reaches as high as  $197\text{--}265 \text{ F g}^{-1}$ , and the normalized capacitance shows a decreasing tendency with the carbonization temperature from  $27.5 \text{ } \mu\text{F cm}^{-2}$  at  $500^\circ\text{C}$  to  $20.2 \text{ } \mu\text{F cm}^{-2}$  at  $900^\circ\text{C}$ . This may be ascribed to the decreased little residual fluorine atoms (1.46–0.28 at%) on the surface of the carbons (Table 1). A little deviation from perfect rectangular shape at lower potential can be observed in CV curves (Fig. 2a) of the carbon, especially for the carbon prepared at lower carbonization temperature, bearing out a few contributions of the pseudo-capacitance by the residual fluorine atoms.

From the view of practical application, the volumetric capacitance of the carbon is a more important parameter for EDLCs [4,5]. As shown in Table 1, the PVDF-derived carbon electrode presents a remarkable high apparent density varying in the range of  $0.801\text{--}0.863 \text{ g cm}^{-3}$ , while that of the activated carbon is generally in the range of  $0.3\text{--}0.5 \text{ g cm}^{-3}$  depend on its surface area and pore size. The high apparent density of the PVDF-derived carbon is ascribed to the lack of activation process and its small pore size. As it possesses both high gravimetric capacitance and

high electrode density, a volumetric capacitance as high as  $218 \text{ F cm}^{-3}$  has been obtained at  $700^\circ\text{C}$ , while the common value of activated carbons is only  $80\text{--}120 \text{ F cm}^{-3}$  [21]. This value is also much higher than that of some reported carbons for high energy supercapacitors, such as the carbide-derived carbon ( $150 \text{ F cm}^{-3}$ ) [22] and high surface-area graphite ( $180 \text{ F cm}^{-3}$ ) [23]. From the view of high capacitance, 0.55 nm may be an optimized pore size for carbons of aqueous EDLCs.

Rate capability is another important feature for supercapacitors. As shown in Fig. 2b, the PVDF-derived ultramicroporous carbons exhibit a moderate rate capability in  $6 \text{ mol L}^{-1}$  KOH aqueous electrolytes. As the current density increases from  $0.05 \text{ A g}^{-1}$  to  $10 \text{ A g}^{-1}$ , the volumetric capacitance of PVFC700 decreased from  $218 \text{ F cm}^{-3}$  to  $110 \text{ F cm}^{-3}$ . Although the capacitance remaining ratio (50.5%) is not as good as some mesoporous carbon or hierarchical porous carbon, the volumetric capacitance of  $110 \text{ F cm}^{-3}$  at  $10 \text{ A g}^{-1}$  is rather a competitive value. If the pore size is a bit of larger, much better rate capability should be obtained but the specific volumetric capacitance may be decreases as a sacrifice.

To evaluate the cycle performances of the PVDF-derived ultramicroporous carbon, galvanostatic charge–discharge cycling was performed at a current density of  $0.5 \text{ A g}^{-1}$  as shown in Fig. 2c. After 1000 cycles, the capacity decay of PVFC700 is only 3% of the initial discharge capacity, indicating the PVDF-derived carbon has a good cycle durability.

As few works have explored the capacitive performances of the carbon with pores smaller than 0.65 nm in non-aqueous electrolytes, it is unknown whether pores with this size are useful for non-aqueous EDLCs. To answer this question, the electrochemical capacitive performances of the PVDF-derived ultramicroporous carbon in  $1 \text{ mol L}^{-1}$   $\text{Et}_4\text{NBF}_4/\text{PC}$  non-aqueous electrolytes were also evaluated in a symmetrical two-electrode cell. Fig. 3 presents the cyclic voltammetry at  $2 \text{ mV s}^{-1}$  and the galvanostatic charge/discharge curves at  $0.05 \text{ A g}^{-1}$  between 0 and 2.5 V. The large deviation from the rectangular shape of the CV curves and linear shape of  $V\text{--}t$  curves indicate the serious polarization of the carbons. The capacitances of the carbons in  $1 \text{ mol L}^{-1}$   $\text{Et}_4\text{NBF}_4/\text{PC}$  calculated by galvanostatic charge/discharge at  $0.05 \text{ A g}^{-1}$  are very small, only  $1.2\text{--}6.6 \text{ F g}^{-1}$ . The ion sizes of desolvated  $\text{Et}_4\text{N}^+$  and  $\text{BF}_4^-$  are 0.68 nm and 0.33 nm, respectively [13]. The poor performances of the carbons in  $1 \text{ mol L}^{-1}$   $\text{Et}_4\text{NBF}_4/\text{PC}$  are attributed to their small pores, which are not accessible even for the desolvated ions. These results give an evidence for confirming that the pore size of the carbon must larger than the desolvated ions for establishing electric double layer capacitance in non-aqueous electrolytes.

The different capacitive behavior of the PVDF-derived ultramicroporous carbon in the aqueous and non-aqueous electrolytes is attributed to the difference in ion dimensions. The pores of 0.55 nm is large enough to be accessible for the hydrated  $\text{OH}^-$  or  $\text{K}^+$  and small enough to ensure a high density, making the PVDF-derived carbon present an outstanding high capacitance in  $6 \text{ mol L}^{-1}$  KOH aqueous electrolytes. However, in  $1 \text{ mol L}^{-1}$   $\text{Et}_4\text{NBF}_4/\text{PC}$  non-aqueous electrolytes, the dimension of the desolvated  $\text{Et}_4\text{N}^+$  and solvated  $\text{Et}_4\text{N}^+$  are 0.68 nm and 1.30 nm [15], respectively, all much larger

**Table 1**  
Microstructure and capacitance of PVDF-derived carbons in  $6 \text{ mol L}^{-1}$  KOH aqueous electrolytes.

Samples	HTT ( $^\circ\text{C}$ )	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$V_t$ ( $\text{cm}^3 \text{ g}^{-1}$ )	Apparent density ( $\text{g cm}^{-3}$ )	F content (at %)	Capacitance		
						( $\text{F g}^{-1}$ )	( $\mu\text{F cm}^{-2}$ )	( $\text{F cm}^{-3}$ )
PVFC600	600	963	0.399	0.801	1.46	265	27.5	212
PVFC700	700	1001	0.403	0.826	0.58	264	26.4	218
PVFC800	800	1012	0.410	0.852	0.39	232	22.9	198
PVFC900	900	976	0.398	0.863	0.28	197	20.2	170

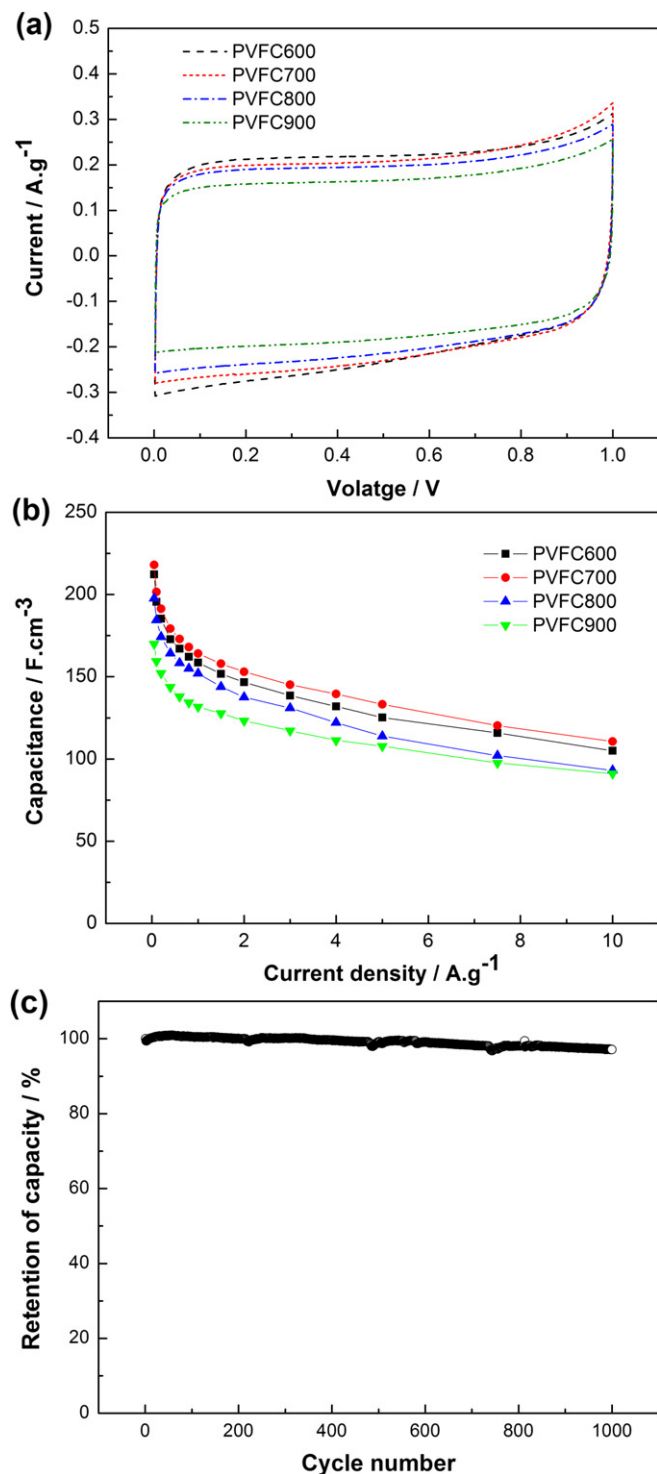


Fig. 2. Electrochemical performances of the PVDF-derived carbons in 6 mol L<sup>-1</sup> KOH aqueous electrolytes, (a) CV curves at a scan rate of 2 mV s<sup>-1</sup>; (b) capacitance as a function of current density; (c) cycle performance of the capacitor based on PVFC700 at a current load of 0.5 A g<sup>-1</sup>.

than the pore size (0.55 nm) of the carbon. That is to say, the pores of the PVDF-derived carbon are too small to be accessible even for the smaller desolvated Et<sub>4</sub>N<sup>+</sup>, leading to a very small capacitance in 1 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub>/PC non-aqueous electrolytes. It confirms that a good match between the pore size of the carbon material and the dimensions of the ions is very important to achieve a high capacitance.

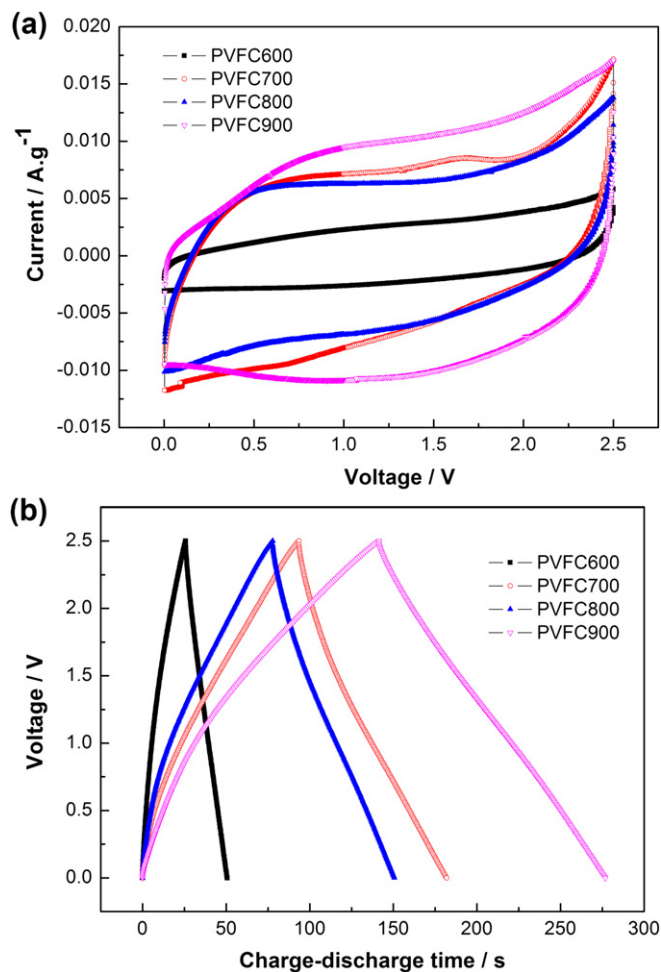


Fig. 3. Electrochemical performances of the PVDF-derived carbons in 1 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub>/PC electrolytes, (a) CV curves at a scan rate of 2 mV s<sup>-1</sup>; (b) galvanostatic charge-discharge curves as a current load of 0.05 A g<sup>-1</sup>.

#### 4. Conclusions

PVDF-derived ultramicroporous carbon with a unimodal pore size of 0.55 nm and a BET surface area of 1012 m<sup>2</sup> g<sup>-1</sup> was investigated as electrode materials for EDLCs with both aqueous and non-aqueous electrolytes. The carbon possesses not only a high gravimetric capacitance (264 F g<sup>-1</sup>) but also a high electric density (0.826 g cm<sup>-3</sup>), resulting in an outstanding high volumetric capacitance of 218 F cm<sup>-3</sup> in 6 mol L<sup>-1</sup> KOH electrolytes. However, the carbon shows only a few capacitances in 1 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub>/PC electrolytes, bearing out that only the pores larger than the desolvated ions are useful.

#### Acknowledgments

This work was financially supported by the National Key Basic Research and Development Program (2009CB220100), the National Science Foundation of China (50802112 and 21073233) and the National High Technology Research and Development Program (2012AA110302).

#### References

- [1] L.L. Zhang, X.S. Zhao, Chem. Soc. Rev. 38 (2009) 2520–2531.
- [2] M. Inagaki, H. Konno, O. Tanaiki, J. Power Sources 195 (2010) 7880–7903.
- [3] B. Xu, F. Wu, R. Chen, G. Cao, S. Chen, Z. Zhou, Y. Yang, Electrochem. Commun. 10 (2008) 795–797.

- [4] E. Frackowiak, *Phys. Chem. Chem. Phys.* 9 (2007) 1774–1785.
- [5] B. Xu, F. Wu, S. Chen, Z. Zhou, G. Cao, Y. Yang, *Electrochim. Acta* 54 (2009) 2185–2189.
- [6] E. Frackowiak, F. Béguin, *Carbon* 39 (2001) 937–950.
- [7] D. Qu, H. Shi, *J. Power Sources* 74 (1998) 99–107.
- [8] H. Shi, *Electrochim. Acta* 41 (1996) 1633–1639.
- [9] A.G. Pandolfo, A.F. Hollenkamp, *J. Power Sources* 157 (2006) 11–27.
- [10] Y.J. Kim, Y. Horie, S. Ozaki, Y. Matsuzawa, H. Suezaki, C. Kim, N. Miyashita, M. Endo, *Carbon* 42 (2004) 1491–1500.
- [11] M. Endo, Y.J. Kim, H. Ohta, K. Ishii, T. Inoue, T. Hayashi, Y. Nishimura, T. Maeda, M.S. Dresselhaus, *Carbon* 40 (2002) 2613.
- [12] P. Simon, Y. Gogotsi, *Nat. Mater.* 7 (2008) 845–854.
- [13] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P.L. Taberna, *Science* 313 (2006) 1760–1763.
- [14] C. Largeot, C. Portet, J. Chmiola, P.L. Taberna, Y. Gogotsi, P. Simon, *J. Am. Chem. Soc.* 130 (2008) 2730–2731.
- [15] J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, *Angew. Chem. Int. Ed.* 47 (2008) 3392–3395.
- [16] B. Xu, S. Hou, M. Chu, G. Cao, Y. Yang, *Carbon* 48 (2010) 2812–2814.
- [17] M.D. Stoller, R.S. Ruoff, *Energy Environ. Sci.* 3 (2010) 1294–1301.
- [18] B. Xu, S. Yue, Z. Sui, X. Zhang, S. Hou, G. Cao, Y. Yang, *Energy Environ. Sci.* 4 (2011) 2826–2830.
- [19] G. Lota, K. Lota, E. Frackowiak, *Electrochem. Commun.* 9 (2007) 1828–1832.
- [20] D. Hulicova-Jurcakova, A.M. Puziy, I. Olga Poddubnaya, F. Suárez-García, J.M.D. Tascón, G.Q. Lu, *J. Am. Chem. Soc.* 131 (2009) 5026–5027.
- [21] B. Andrew, *Electrochim. Acta* 53 (2007) 1083–1091.
- [22] J. Chmiola, G. Yushin, R. Dash, Y. Gogotsi, *J. Power Sources* 158 (2006) 765–772.
- [23] H.Q. Li, Y.G. Wang, C.X. Wang, Y.Y. Xia, *J. Power Sources* 85 (2008) 1557–1562.